Indian J. Phys. **75A** (4), 301-305 (2001)

IJP A
— an international journal

Electronic and vibronic interactions in the mixed valence dimers

S M Ostrovsky[a], K Nag[b] and W Haase[a]*

[a] Institute of Physical Chemistry, Darmstadt University of Technology, Petersenstraße 20, D-64287 Darmstadt, Germany
[b] Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700 032, India

E-mail : d54d@hrzpub.tu-darmstadt.de

Abstract : A general overview of different electronic and vibronic interactions in the mixed valence dimeric compounds is presented. They are isotropic exchange interaction, double exchange and vibronic coupling (PKS and Piepho modes). The influence of these interactions on the properties of the dimeric complexes is discussed. As an example we present our investigations of fully delocalized $[L^1Fe_2(\mu\text{-}OAc)_2](ClO_4)$ iron dimer.

Keywords : Mixed valence dimers, electronic and vibronic interactions.

PACS No. : 33.20.Wr

1. Introduction

Mixed-valence (MV) transition metal clusters are of great interest because of their unusual spectral and magnetic properties and the possibility to use these properties for studying the intramolecular electron transfer process in many biologically important compounds [1,2]. For instance, valence delocalized $[Fe_2S_2]^+$ pairs where iron is in the formal oxidation state + 2.5 were found in a variety of iron-sulfur clusters in ferredoxins. Because of this, a growing interest in the characterization, the modelling as well as in the theoretical description of such compounds exists [3-6].

MV dimers are very convenient systems for better understanding of the electron delocalization process because of the possibility to take into account all relevant interactions. In this paper we briefly discuss some of these interactions and their influence on the properties of the dimeric MV compounds.

2. Theoretical background

Double exchange :

The conception of double exchange was suggested by Zener [7] for explanation of the ferromagnetism observed in some MV manganites of perovskite structure. The double exchange interaction involves the coupling of two localized magnetic moments through the migration of the itinerant extra electron. According to the Hund rule, a high spin configuration on each spin core is more preferable from the energetic point of view. The process of migration does not change the orientation of the extra electron. So the transfer process is spin dependent and much more efficient in the case when spins of interacting ions are parallel. Double exchange results in a strong spin polarization effect which favours a ferromagnetic spin alignment. A general solution of the double exchange problem for MV dimers was suggested by Anderson and Hasegawa [8]. The expression for the double exchange splitting of a MV dimer has the following form :

$$E(S) = \pm t \frac{S+1/2}{2S_0+1} \qquad (1)$$

where t is the electron transfer integral, S_0 means the spin of each interacting ions without extra electron (spin core) and S is the total spin of the system. We prefer to use eq.(1) in another form :

$$E(S) = \pm B(S+1/2), \qquad (2)$$

where $B = t/(2S_0+1)$ is the double exchange parameter for the regarded complex. One can see that the energy splitting due to the double exchange interaction is linear in S and maximal for the maximal value of the total spin of the system. Strong double exchange in the dimeric complexes always results in the ferromagnetic ground state independently of the sign of the double exchange parameter and the sign of the isotropic exchange interaction. This situation is shown in Figure 1 where

* Corresponding Author

the energy levels of the $d^1 - d^2$ MV dimer are presented in the case of antiferromagnetic isotropic exchange and strong double exchange interaction.

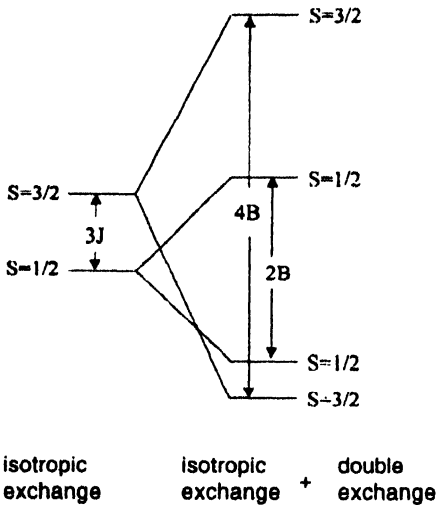

Figure 1. Energy levels of the delocalized $d^1 - d^2$ MV dimer.

Vibronic interactions : PKS model :

The moving electron strongly perturbs the ligand environment so the vibronic coupling plays a considerable role in MV systems along with isotropic and double exchange interactions. The background for the consideration of the vibronic effects in this kind of systems was suggested by Piepho, Krausz and Schatz and became well-known as the PKS model [9-11]. It is assumed that the subunits have the same point group symmetry in both oxidation states (with and without extra electron), so only totally symmetric normal coordinates q_A and q_B associated with each subunit are regarded. The new collective coordinates are then expressed as :

$$q_{\pm} = \frac{1}{\sqrt{2}}(q_A \pm q_B). \qquad (3)$$

The "in-phase" q_+ mode decreases and increases the potential energy of both subunits at the same time. So it does not affect the extra electron migration and can be excluded from the consideration. On the contrary, the "out-of-phase" q_- mode is relevant to the electron transfer process. Depending on the sign of q_-, the nuclear displacements stimulate the location of the extra electron on one of the ions (A or B). The opposite sign of q_- mode promotes the location of the extra electron on another subunit. Vibrational coordinate $q_- \equiv q$ for two coupled octahedral centres is shown in Figure 2.

The adiabatic potentials relating to a given full spin S of the system have the following form :

$$U_{\pm}^S(q) = -JS(S+1) + \omega q^2/2 \pm \left[(B(S+1/2))^2 + v^2 q^2\right]^{1/2}, \qquad (4)$$

where ω is the frequency of PKS out-of-phase mode, v is the vibronic coupling parameter. Depending on the relationship between double exchange parameter and vibronic coupling with the PKS out-of-phase mode there are three different type of the

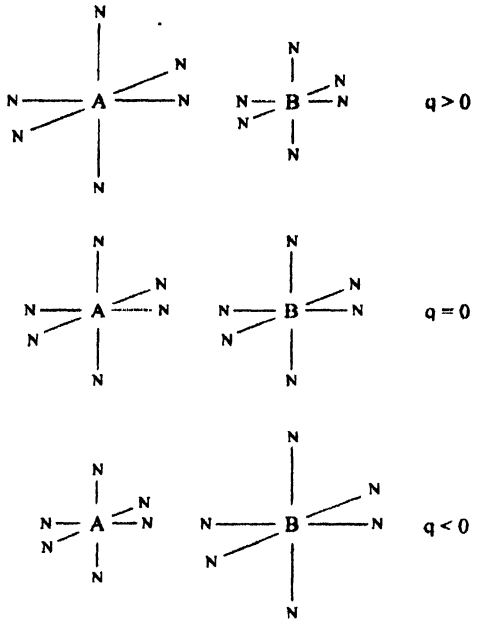

Figure 2. Vibrational coordinate q for two coupled octahedral centres

adiabatic curves (Figure 3). When the double exchange is negligibly small compared with the vibronic interaction $\left(B(S+1/2) << v^2/\omega\right)$, the potential curve U_-^S has two well separated minima (Figure 3a). The wave functions in these

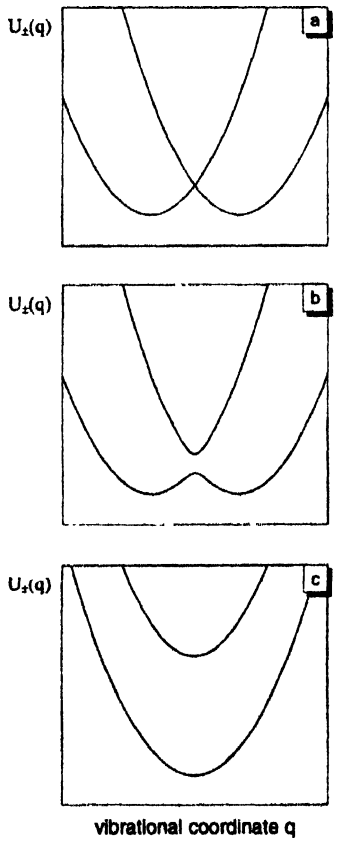

Figure 3. Potential energy curves for a mixed valence dimers with diamagnetic cores : (a) class I, (b) class II and (c) class III systems.

minima correspond to a localization of the extra electron on one of the subunits. The system is fully localized (class I in Robin and Day classification scheme). With the increasing of the double exchange interaction the barrier between these minima becomes lower. In the case when $B(S+1/2) < \nu^2/\omega$ the electron transfer process is possible but requires an activation energy. This situation is shown in Figure 3b and corresponds to the class II in Robin and Day scheme. And finally, in the case of weak vibronic interaction (or strong double exchange) when $B(S+1/2) > \nu^2/\omega$ the potential curve U_-^S has one minimum at the position $q = 0$ and the extra electron is fully delocalized (class III system). So the PKS interaction produces a localization effect. It should be mentioned that this kind of interaction is independent of the total spin of the system whereas the value of the double exchange interaction decreases with the total spin decreasing. The smaller the value of the total spin of the system the more localized the itinerant extra electron is.

Vibronic interactions : Piepho type of vibrations :

The PKS model is not the only possibility to take into account vibronic interactions in MV systems. Piepho [12, 13] suggested a new vibronic coupling model for these type of compounds. Piepho type of vibrations change the metal-metal distances and result thus in the modulation of the value of the transfer integral. One can expand the double exchange parameter in the Taylor series and obtain in the first approximation :

$$B(r) = B(r_0) + \left(\frac{\partial B}{\partial r}\right)_{r=r_0} Q, \qquad (5)$$

where r is the metal-metal distance, r_0 is the metal-metal distance for the system without the itinerant extra electron, Q is the vibrational coordinate in the Piepho model, $\lambda_0 = -(\partial B/\partial r)r = r_0$ is the vibronic coupling parameter with the P-vibrations. It should be mentioned that the effective (multielectron) P-coupling parameter $\lambda(S) = \lambda_0(S+1/2)$ possesses the same spin dependence as the double exchange.

The problem of localization-delocalization in the dimeric MV clusters in the presence of both type of vibrations (PKS and Piepho) was studied in Ref. [14]. In the framework of semiclassical adiabatic approach, the potential surfaces were analysed. The adiabatic potentials relating to a given full spin S of the system have the following form :

$$U_\pm^S(q,Q) = -JS(S+1) + (\omega q^2 + \Omega Q^2)/2 \pm$$

$$\left[\left(B(S+1/2) - \lambda_0(S+1/2)Q\right)^2 + \nu^2 q^2\right]^{1/2}, \qquad (6)$$

where Ω is the frequency of Piepho type of vibrations.

Depending on the relationship between the key parameters of the dimeric MV system several qualitatively different types of the adiabatic surfaces were found.

In the case of strong PKS coupling $\left(\nu^2/\omega > \lambda^2(S+1/2)^2/\Omega\right)$, the behaviour of the system as well as the shape of the adiabatic surfaces depend on the value of the double exchange parameter. Comparatively, weak double exchange $\left(B(S+1/2) < \nu^2/\omega - \lambda^2(S+1/2)^2/\Omega\right)$ corresponds to the adiabatic potential U_-^S with two equivalent minima in qQ-plane (Figure 4). These minima are symmetric in the q-subspace and shifted along Q axis in the negative direction. The extra electron in these minima is partially localized and the degree of localization depends on the relationship between the key parameters. With the increase of the double exchange, these two minima move toward the Q axis, the barrier between them becoming lower (Figure 4). The extra electron becomes more and more delocalized. Under the condition $B(S+1/2) = \nu^2/\omega - \lambda^2(S+1/2)^2/\Omega$, the minima are transformed into one minimum in which the extra electron is fully delocalized. So in the case of strong PKS coupling depending on the magnitude of the double exchange, MV dimer can belong to class I, II or III in Robin and Day classification scheme.

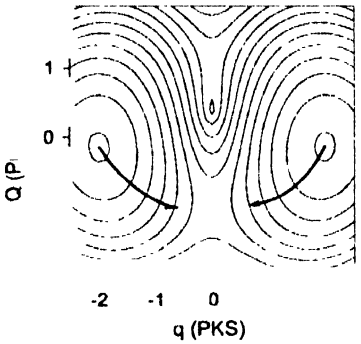

Figure 4. The contour plot of the lower sheet $U_-^S(q,Q)$ for a mixed valence dimer. Case of strong PKS coupling (arrows show the displacements of the minima position with the double exchange increasing).

Case of strong Piepho coupling $\left(\nu^2/\omega < \lambda^2(S+1/2)^2/\Omega\right)$:

As it was shown in Ref. [14], under this condition, the system is fully delocalized independently of the relative values of the double exchange and PKS coupling. The MV dimer belongs to class III even providing small magnitude of the double exchange. The molecular vibrations effectively enhance the double exchange giving rise to a strong ferromagnetic contribution.

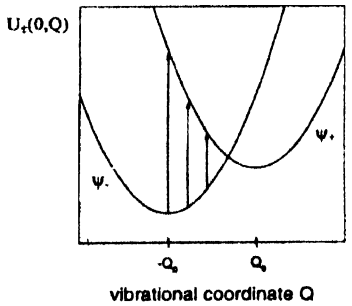

Figure 5. Scheme of the intervalence absorptions (vertical section of the adiabatic surfaces along the Q-axis).

The correlation between the degree of delocalization and parameters of intervalence absorption band in the presence of both type of vibrations differs from that for PKS model. In the pure PKS model the system of class III exhibits strong narrow intervalence band and as a consequence the optical properties of some real compounds cannot be explained in the framework of this model. In case of taking into account both type of vibrations the fully delocalized system can exhibit strong broad intervalence band if Piepho coupling is dominant. The broad band arises from the transitions between fully delocalized states (Figure 5).

3. Data analysis

To the best of our knowledge, there exist only a few examples of class III valence delocalized dinuclear iron complexes. During past years, we reported theoretical and experimental investigations of $[L^1Fe_2(\mu-OAc)_2](ClO_4)$ iron dimer [15-18]. The Mössbauer spectrum of this compound shows extra electron delocalization in the whole temperature range. The optical absorption spectra were recorded in the temperature range 85 – 300 K. A strong broad intervalence band was found at about 8800 cm^{-1}. Magnetic measurements of the investigated complex show a ferromagnetic ground state (S=9/2). It is well known that in this type of systems the isotropic exchange interaction is antiferromagnetic, so the presented magnetic properties are a result of a strong double exchange interaction. For details of the experiments, we refer to Refs. [15, 16].

The first theoretical explanation of the observed experimental behaviour was given in Ref. [15] without any vibronic coupling. From the position of the maximum of the intervalence absorption band, the value of the double exchange parameter was found to be 880 cm^{-1}. At this given value of the double exchange the magnetic measurements allow us to estimate the magnitude of the isotropic exchange parameter. Strong double exchange results in ferromagnetic ground state and even at room temperature, the behaviour of the complex is still determined by this ground state only.

At the next stage of the investigation, we introduced the consideration of vibronic coupling with PKS out-of-phase mode [17]. It was shown that the behaviour of the system is determined by a strong competition between two main processes : double exchange interaction and vibronic interaction of PKS type. The former leads to delocalization of the itinerant electron while the latter represents a trapping effect that tends to localize the extra electron. The position and the shape of intervalence absorption band were calculated using standard quantum mechanical methods. In the presence of vibronic coupling with the PKS out-of-phase mode, the position of the maximum of the intervalence absorption band does not correspond anymore to the $2(S_{gr} + ½)$ values of the double exchange parameter. To explain the physical properties of the system, in this case we need a smaller B-value. We obtained B = 820 cm^{-1} for presented compound [17] (compared with 880 cm^{-1} at the previous stage of consideration [15]).

As mentioned above, it is impossible to obtained a broad intervalence band for the fully delocalized compound (Class III) in the framework of pure PKS model. The investigations of the regarded complex on the basis of the generalized vibronic model are presented in Ref. [18]. A very good agreement between experimental absorption band and theoretical curve was obtained at the following set of parameters : $B = 260\ cm^{-1}$, $\omega = 310\ cm^{-1}$, $\nu = 3\ \omega$, $\Omega = 125\ cm^{-1}$, $\lambda_0 = \Omega$. The obtained B-value is the double exchange parameter for the system with metal-metal distance equal to that in the complex without extra electron. The moving electron changes this distance and real (effective) double exchange parameter can be calculated using eq. (5). One can see that S = 9/2 ground state corresponds to a case of strong Piepho coupling $\left(\nu^2 / \omega < \lambda^2 (S+1/2)^2 / \Omega\right)$. The adiabatic surface possesses single minimum in which the extra electron is fully delocalized. The effective value of double exchange in this minimum is 880 cm^{-1}, the same as that obtained from the maximum of the intervalence absorption band at the first stage of investigations [15]. Decrease of the total spin value leads to the reduction of the magnitude of double exchange as well as vibronic coupling of Piepho type. The S = 1/2 state corresponds to the case of strong PKS coupling. The adiabatic surface has two deep minima in which the extra electron is localized. So the population of the excited spin states leads to localization of the itinerant extra electron. But the combined effect of double exchange and strong Piepho vibrations results in ferromagnetic ground state well isolated from the excited ones. The behaviour of the complex is determined by this ground state only and the system is fully delocalized in the whole temperature range.

4. Concluding remarks

As one can see the most detailed description of the MV compound is possible only in the framework of generalized vibronic model which takes into account both type of vibrations. It should be mentioned that although we have many parameters in the present model (double exchange, vibronic coupling parameters with PKS and Piepho vibrations), all of them can be more or less accurately obtained from the comparison between the experimental and theoretical data because their influence on the position and the shape of the intervalence absorption band and the degree of delocalization of the itinerant extra electron is different (see Table 1). The increase of all of these parameters

Table 1. The effects of double exchange, PKS and Piepho vibronic coupling on the shape and the position of the intervalence absorption band (IAB) and the degree of delocalization of the itinerant extra electron.
I = increase and D = decrease

	Energy of the maximum of IAB	Width of IAB	Degree of delocalization
B (double exchange)	I	D	I
ν (PKS)	I	I	D
λ_0 (Piepho)	I	I	I

shifts the position of the maximum of the intervalence band to the high energy region but the bigger value of the double exchange results in smaller band width while the growth of coupling parameters leads to broad band contour with the degree of delocalization decreasing in the case of PKS vibrations and increasing for the Piepho vibrations.

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft (DFG) for financial support.

References

[1] E L Bominaar, C Achim, S A Borshch, J-J Girerd and E Münck *Inorg. Chem.* **36** 3689 (1997)

[2] C Achim, E L Bominaar, E Münck *J. Biolnorg. Chem* **3** 126 (1998)

[3] V Papaefthymiou, J-J Girerd, I Moura, J J G Moura and E Munck *J. Am. Chem. Soc.* **109** 4703 (1987)

[4] L Noodleman and D A Case *Adv. Inorg. Chem* **38** 423 (1992)

[5] D R Gamelin, E L Bominaar, M L Kirk, K Wieghardt and E I Solomon *J Am. Chem Soc* **118** 8085 (1996)

[6] D R Gamelin, E L Bominaar, C Mathoniere, M L Kirk, K Wieghardt, J-J Girerd and E I Solomon *Inorg Chem.* **35** 4323 (1996)

[7] C Zener *Phys Rev* **82** 403 (1951)

[8] P W Anderson and H Hasegawa *Phys. Rev* **100** 675 (1955)

[9] S B Piepho, E R Krausz and P N Schatz *J Am Chem Soc* **100** 2996 (1978)

[10] P N Schatz in · D B Brown (ed), *Mixed Valence Compounds (NATO ASI Series)* (Dordrecht D Riedel) p 115 (1980)

[11] K Y Wong and P N Schatz *Prog Inorg Chem* **28** 369 (1981)

[12] S B Piepho *J Am. Chem Soc* **110** 6319 (1988)

[13] S B Piepho *J Am Chem. Soc* **112** 4197 (1990)

[14] J J Borras-Almenar, E Coronado, S M Ostrovsky, A V Palii and B S Tsukerblat *Chem Phys.* **240** 149 (1999)

[15] C Saal, S Mohanta, K Nag, S K Dutta, R Werner, W Haase, E Duin and M K Johnson *Buns Ber Phys. Chem.* **100** 2086 (1996)

[16] S K Dutta, J Ensling, R Werner, U Flörke, W Haase, P Gutlich and K Nag *Angew. Chem* **109** 107 (1997)

[17] S M Ostrovsky, R Werner, K Nag and W Haase *Chem. Phys Lett* **320** 295 (2000)

[18] S M Ostrovsky, K Nag and W Haase (to be published)